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GENERATION OF INTERNAL STRESS IN THE PROCESS OF
SOLIDIFICATION OF SYNTHETIC RESIN, II

Internal Stress caused by Shearing Force

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Experiments were planned to ascertain the residual stress occurring in amorphous solid of high polymer. For this, injection molded articles of α -methylstyrene-styrene copolymer and bis-phenol-polycarbonate were used, and dilatometric measurement on the pellet form of the polymers and measurements on heating deformation were adopted.

As the results, it is clarified that deformation by residual stress begins to occur at the lower limiting temperature of 2nd order transition region, and considering the activation energy of deformation calculated from rate constants of experimental deformation, the residual stress may be due to the orientational configuration of polymer molecules by molten flow at the injection procedure.

Introduction

Residual stress, which is considered to occur in solid metal or ionic crystal, has been explained by the theory of lattice defect, dislocation and crystal transformation, *etc.* based upon thermal analysis or X-ray diffraction.

However, solid of high polymer, even though it is crystalline polymer, has the structure in which crystal region such as spherulite is dispersed in amorphous region. In other high polymers their structures are amorphous, and accordingly the residual stress in them cannot be treated by the theory of crystallite. Nevertheless, from the industrial point of view, the residual stress in molded articles of high polymer originated through various forming procedures causes the lowering of mechanical strength and in extreme case it is considered to give rise to cracks and fractures, *etc.* Therefore, it is important to make clear what it really is and how the residual stress corresponds to the molecular structure of high polymer. From this standpoint, it is performed, in the present investigation, to determine the temperature, at which the residual stress in injection molded form of amorphous linear polymers obtained by rapid cooling of molten flow under high shearing force will be released, and to determine how the procedure of the release can be treated by the kinetic theory. From these results it is attempted to make clear to what part of configurational structure of high polymer the residual stress is related.

Residual stress in high polymer solid can be investigated by applying polarized photo-elasticity, but for the use of this method, the polymer must be transparent and moreover have suitable polarized photo-elastic coefficient. Thermal analysis is an effective method for investigating the

residual stress on metal or graphite *etc.*, but as the heat content of organic polymer is large compared with energy of the residual stress, and the heat conductivity is low, it is considered that thermal analysis is difficult on the stress of organic polymer. However, when the residual stress exists in solids especially of high polymers, it will be released and deformation will be caused by heating the solids, and so the residual stress can be grasped from the deformation by heating. In this research, it has been decided to adopt this method.

As the testing materials of amorphous linear polymer solid, α -methylstyrene—styrene copolymer and *bis*-phenol-polycarbonate were used. First, as for the pellet form of the testing material, the specific gravity-temperature relations were obtained by the dilatometry, using a glass tube and mercury. Taking specimens from the injection molded testing material, which is thought to have residual stress by rapid cooling under high shearing force, the relations between deformation and temperature were obtained by heat treatment of these specimens at various temperatures, and then the temperature, at which the release of residual stress began to arise, was obtained. Next, the rates of this deformation with time were obtained, and from this relation the rate constant of the deformation was calculated. Further from the relation between the rate constant and temperature, the activation energy for the deformation was calculated.

In the near future polarized infrared absorption spectrum will be measured about the injection molded testing materials to ascertain variations of molecular structure accompanying the release of residual stress.

Experimentals

Testing materials The testing materials used in these experiments were as follows:

- (1) *α -methylstyrene-styrene copolymer* Viscosity average molecular weights according to viscometrie of benzene solution was 140,000, when a formula $(\eta)_0 = KM^\alpha$ was used at 30°C, between intrinsic viscosity $(\eta)_0$ and molecular weight M , where $K = 0.97 \times 10^{-4}$, and $\alpha = 0.74$ were postulated. Weight ratio of α -methylstyrene to styrene is about 25:75. (Dow Chem. Styron #700)
- (2) *Bis-phenol-polycarbonate* Average molecular weight was 30,000. (Bayer, Makrolon E)

Method of measurement on the relation between specific gravity and temperature

The testing materials were extruded, after heated to molten flow by extruder, and cut to pellet form and then cooled. For the testing material (1), pellets were dried in vacuum for 24 hours at room temperature, and for the testing material (2), they were dried in vacuum for 30 hours at 60°C. The specific gravity and temperature relations were obtained using a dilatometer which shows the expansion of testing materials as expansion of mercury column in the capillary tube connected to glass tube. This dilatometer was made to be able to carry out heating, cooling and constant temperature treatment in a double thermostat, by which the temperature maintenance was within $\pm 5/1000^\circ\text{C}$.

First, the pellet formed testing material was packed in the glass tube, and after air was evacuated by an oil diffusion pump and replaced with mercury, the temperature was raised up to 120°C for the testing material (1) and up to 160°C for the testing material (2) at the rate of

about 1°C per minute and lowered at the same rate. The temperature was kept constant for 30 minutes at each experimental point during the experiment, and the relations between the specific gravity and the temperature were measured from the height of mercury column in consideration of expansion of glass, etc. The relations obtained were found to have a 2nd order transition region for both testing materials, and above and below the region the relations were roughly linear respectively and also maintaining the temperature near this transition region, no variation of specific gravity with time was observed for about 3 hours.

Method of measurement on relation between heating deformation and temperature With α -methylstyrene—styrene copolymer, the plate formed specimens of 58×123 mm with 2 mm thickness which had the residual stress caused by injection molding machine was taken as the testing piece and heating deformations in the direction of molten flow and also heating deformation perpendicular to it were measured. Also with polycarbonate, the molded articles of 10×12×90 mm rectangular form were taken as the specimens. These specimens were heated for about 8 hours at several points of temperature above and below their 2nd order transition point described in the previous item and deformations were measured and the relations between the heating deformation and the temperature were obtained.

Method of measurement on heating deformation rates α -methylstyrene—styrene copolymer plate formed specimens were heated at 3 points of temperatures, namely 105, 110 and 115°C. They were the upper limiting temperature of the 2nd order transition region, and slightly higher points than the temperature respectively.

For these cases, the rates of deformation with time were measured by the same method described above, until deformation could not be observed any more.

Results

Relations between specific gravity and temperature For α -methylstyrene—styrene copolymer and *bis*-phenol-polycarbonate, the relations between specific gravity and temperature are the same by both cases, namely by temperature raising and temperature lowering, and they are as shown in Figs. 1 and 2 for each material. As can be seen from these, for α -methylstyrene—styrene copolymer, 2nd order transition point is 96°C and 2nd order transition region 81°C~105°C, and for *bis*-phenol-polycarbonate, the point is 135°C and the region 128°C~138°C.

Relations between heating deformation and temperature As for various points of α -methylstyrene—styrene copolymer and *bis*-phenol-polycarbonate, the relations between heating deformation for 8 hours and temperature are shown in Figs. 3 and 4 for each material. The deformation were shrinkage or expansion depending on the direction parallel or perpendicular to that of molten flow of the polymer. From these, it can be seen that the deformation begins nearly at the lower limit of 2nd order transition region and becomes to be remarkable at the 2nd order transition point.

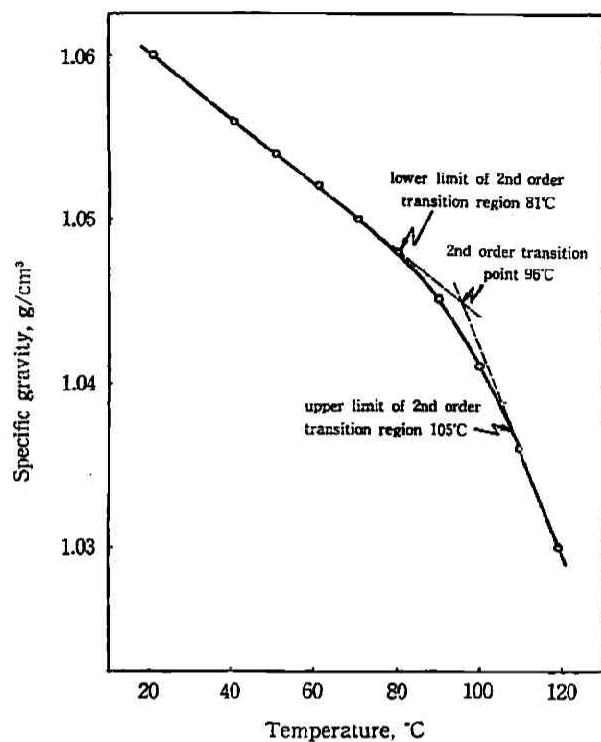


Fig. 1 Relations between specific gravity and temperature on α -methylstyrene-styrene copolymer

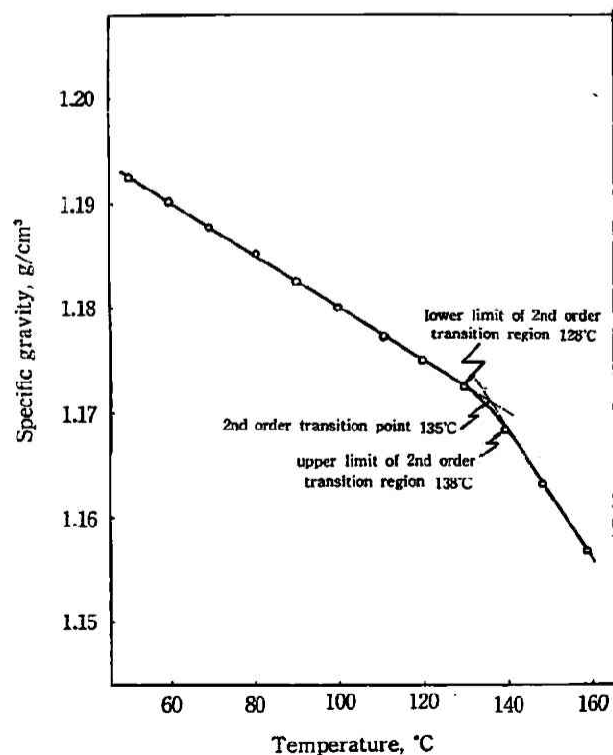


Fig. 2 Relations between specific gravity and temperature on bis-phenol-polycarbonate

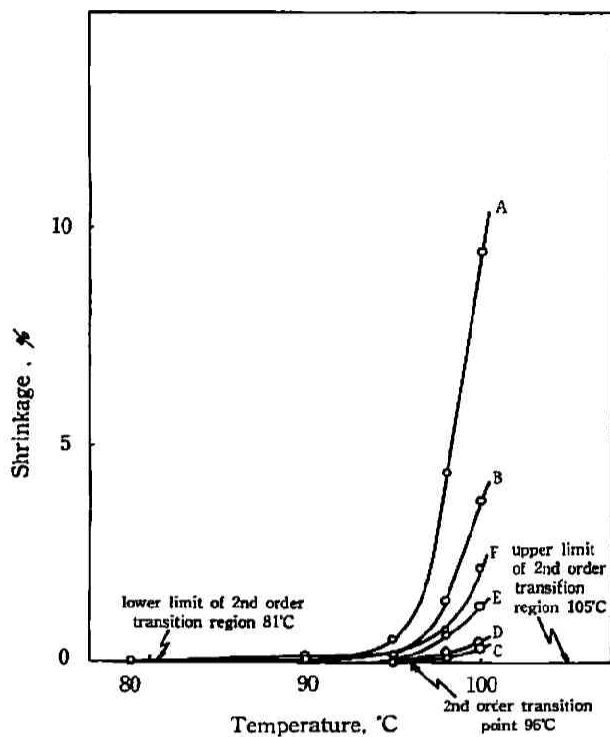


Fig. 3 Relations between heating deformation and temperature on α -methylstyrene-styrene copolymer (heating for 8 hours) (A~F show measuring points.)

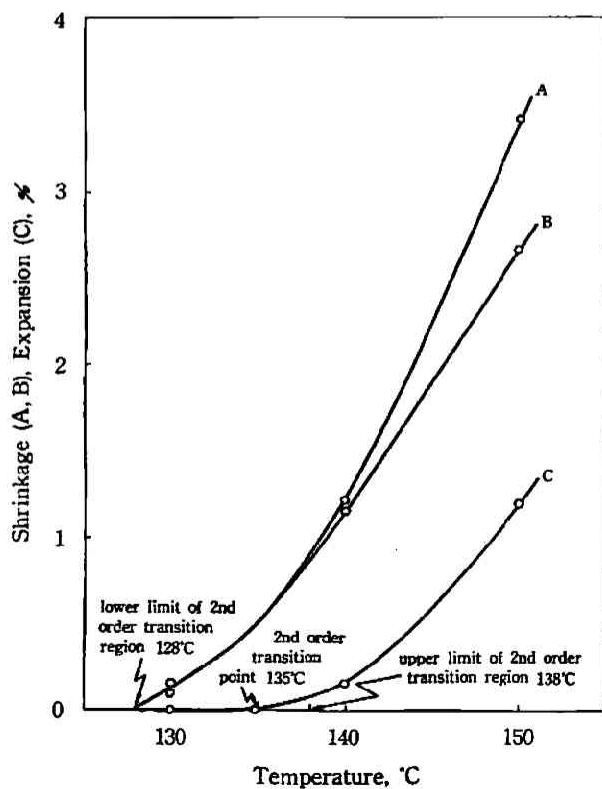


Fig. 4 Relations between heating deformation and temperature on α -methylstyrene-styrene copolymer (heating for 8 hours) (A, B and C show measuring points.)

Heating deformation rates For α -methylstyrene-styrene copolymer specimens, the result on heating deformation rates is shown in Fig. 5, where notation \parallel is parallel to the flow direction of molten-resin and notation \perp is perpendicular to it, and $(-)$ shows contractions and $(+)$ shows expansions. Final deformations were almost the same for the 3 points of temperature, namely 105, 110 and 115°C.

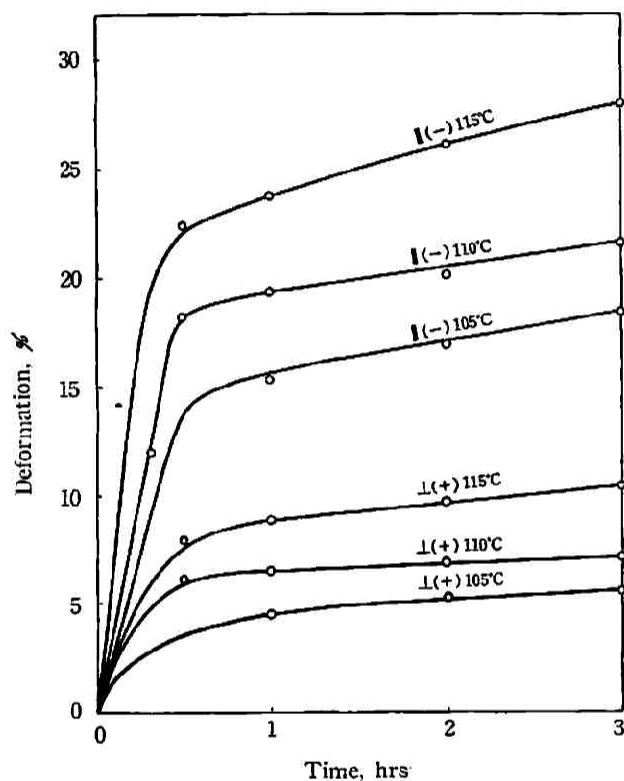


Fig. 5 Heating deformation rates on α -methylstyrene-styrene copolymer

\parallel : parallel to molten flow
 \perp : perpendicular to molten flow
 $(-)$: shrinkage
 $(+)$: expansion

Considerations

As the results of the experiment interesting knowledge on the residual stress was obtained by injection molding of the amorphous linear polymers, such as α -methylstyrene-styrene copolymer and polycarbonate, which were molten and rapidly cooled under high shearing force.

First, it has been clarified according to the dilatometry on pellet formed testing materials that regardless of raising or lowering of temperature, the relations between specific gravity and temperature are the same as shown in Figs. 1 and 2, and that 2nd order transition region exists.

Secondary, variation of specific gravity is not observed within experimental error, by heating for a long time at the same temperature in this region, and so regardless of whether the residual stress is present or not, the relations between specific gravity and temperature are the same.

Next, it has made clear from the results of Figs. 3 and 4 that in the relation between

temperature and deformation appeared by the release of the residual stress by heating, the deformation starts at the lower limiting temperature of the 2nd order transition region and becomes remarkable at the transition point.

This fact is markedly important to know the endurance temperature of injection molded article, and at least it can be said that the molding articles of amorphous polymer, having the residual stress, can be used without the occurrence of deformation below the lower limit of the 2nd order transition region measured by the dilatometry.

As in this 2nd order transition region the residual stress which has been restrained in the amorphous high polymer is released and causes the deformation, it can be presumed that the change of inner structure of high polymer solid at this temperature region is that of molecular arrangement or molecular structure. For α -methylstyrene—styrene copolymer, the heating deformation rates with time at the temperature slightly above the 2nd order transition region are shown in Fig. 5 and the deformations finally reach the same value in this region. The rate constants of deformation calculated from these rates proved to be of 1st order rate and from this, the relation between $\ln k$ and $1/T$ is shown in Fig. 6 and the activation energy of deformation is calculated to be 13~16kcal/mole by the formula $k=e^{-K/RT}$.

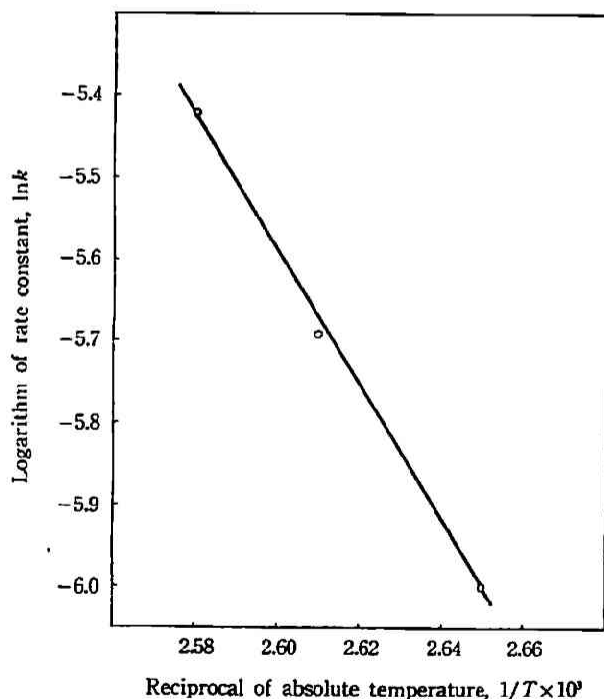


Fig. 6 Relation between logarithm of rate constant and reciprocal of absolute temperature

However, it is considered that the molecular structure corresponding to the state having residual stress in amorphous polymer has some sorts of molecular restraint or deviation from the normal molecular configuration and for this the following various molecular restraints or deviations

exist in the polymer. That is, the molecular entanglement, orientation of the molecular chain, the elongation and contraction of the molecular chain from an equilibrium state, the intermolecular Van der Waals force *etc.* may be some of the restraints, and in high polymer it is hard to consider the variation of bond length or bond angle as the restraint because of their rigidity compared with the above mentioned factors. Of these, the energy necessary to break carbon—carbon chain by molecular entanglement is some eighty kcal/mole, and the Van der Waals force is about 1~2 kcal/mole. Comparing these values with the above stated activation energy necessary for releasing the residual stress, the Van der Waals force alone is too small, the breaking of carbon—carbon chain too large, and after all the activation energy of collapse of orientation, elongation from contracted molecular chain or contraction from elongated chain can be considered to correspond appropriately to the experimental result.

That is, in the molded articles with residual stress, it is considered that the molecules in molten flow are cooled rapidly under high shearing force and are taking unstable orientational structure at room temperature, that is to say in the direction of molten flow the molecules exist in the elongated state of chain and in the perpendicular direction to it in the contracted state of chain. And by heating it above the 2nd order transition temperature, at which the thermal movement of the high polymer becomes active, orientational configuration may diminish, because it has a tendency to approach stable molecular chain arrangement and as the result, the deformation arises from the molded form in which the stress still remains. It is also reasonable that the release of restraint by the Van der Waals force contributes to this deformation, but considering from the value of activation energy, at least, the above-mentioned transition may be main phenomena.

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